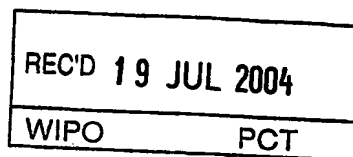




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20033110

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2004.07.13

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03-07-07*20033110

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KR/HBS/107867

2003/07/07

2003-07-07

Patent Application No.: (new)

Applicant: Sinvent AS

Title: "Method of production for gas diffusion electrodes"

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INTRODUCTION

The invention relates to a method and an apparatus for manufacturing a gas diffusion electrode. Uses of the electrode are also described. In a special embodiment, the electrode is a plastic bounded thin gas diffusion electrode with high catalytic activity for the oxygen or the hydrogen reaction.

BACKGROUND

Gas diffusion electrodes have been developed for a large number of fuel cell applications and for metal-air battery systems. The most common electrodes are based on Polytetrafluoroethylene (PTFE) and activated carbon. The high surface area carbon is used as support for a noble or non-noble catalyst. Alternatively, unsupported catalyst can be distributed inside the electrode. The PTFE binds the electrode together and increases the hydrophobicity of the electrode to prevent liquid flooding of the channels for gas transport. Often a metal mesh is present in the electrode as current collector and/or for mechanical strength.

Two methods have been developed to form mechanical stable electrodes from powders, the wet method and the dry method.

The preparation of the active material and the binder mixture can take place by a 'wet' process. This involves introducing the active material and the binder in an organic solvent or water. The slurry is then stirred and a homogeneous mass exists. Some solvent can also be evaporated by heat treatment. After the electrodes have been calendared and/or pressed into a thin sheet the electrode has to be dried for removal of the last remains of the solvent.

In US 3,457,113 and US 3,706,601 it is known that the binder can be introduced from an aqueous or organic suspension. In this case further heat treatment is required to remove surfactants (wetting agents) used in the PTFE suspension. To remove the wetting agents from the electrode a temperature of over 200 °C is used. At temperatures of more than 300 °C a nitrogen atmosphere is required to prevent oxidation. These temperature steps severely hamper a continuous production line of electrode manufacturing. The electrodes must be heated at a rate

< 6 ° / min to prevent cracking of the electrode structure. In addition, the required temperature must be kept for at least 1 hour to be certain that all the surfactants have evaporated. Therefore, the best method for heat treatment is by inserting a batch in a closed furnace. A furnace connected to a continuous production line will
5 be very expensive and a rate determining step for the total production capacity of the line.

In the German patent publication (Offenlegungsschrift) 2,161,373 the carbon powder and PTFE powder is mixed in dry state to form agglomerate. The dry mixture
10 is immediately thereafter pressed onto the metallic-supporting member. In so doing there is avoided any heat treatment having as its objective the plastifying of the plastic in order to strengthen the electrode. Accordingly, the procedure described in German patent publication (Offenlegungsschrift) No. 2,161,373 has the advantage of requiring little technological effort. In addition, there are obtained elec-
15 trodes of good electrochemical activity because of the absence of elevated temperatures and because there does not take place coverage of any unnecessary large surface of the mass particles by plastified binders. In the US patent 4,336,217 a method for preparing the agglomerate from the powder is given. By using a specially designed paddle mixer with an incorporated cutting head with sharp knives the
20 PTFE and carbon powders is mixed homogeneously preventing the dry mixture to adhere and clump together.

In German patent publication (Offenlegungsschrift) No. 2,161,373 and US patent 4,336,217 above the agglomerate formed is treated in the dry form. This causes
25 the thin sheet to easily break and the handling of the electrode is difficult. Only a limited number of active carbon powders give the agglomerate sufficient mechanical strength to produce the electrodes.

The dry and the wet preparation methods have advantages and disadvantages.
30 With the wet method the plastifying qualities of the agglomerate simplifies the calendering step in the electrode production. However, the surfactants acting as wetting agents can only be removed by additional heat treatment. This is problematic for a continuous production line as described above. In the dry method heating is not necessary in the electrode production. However, for the dry method the callen-

dering of the agglomerate to form a thin sheet is problematic. Several callendering steps are required with careful control of the product in order to prevent the thin sheet from cracking and breaking apart. The method is therefore best suited for a batch production line and not in continuous production.

5

In the US patent 5,312,701 an alternative production method is shown. The active layer where the reaction take place and the gas diffusion layer of the electrode are prepared by the filtration method in a single pass process. It is claimed that this is a quicker and more cost-effective method. However, the electrodes have to be
10 heated to 270 °C under pressure in a sintering procedure after the electrodes have been produced. This is a time consuming and slow step that is not well suited for continuous production.

SUMMARY OF THE INVENTION

15 It is an objective of the invention to provide a process for production of thin hydrophobic gas diffusion electrodes which is suitable for continuous production lines and significantly freer form of the above mentioned problems.

In a first aspect the invention provides a method of manufacturing a gas diffusion
20 electrode, the method comprising: agglomerating a powder mixture with PTFE particles in a dry form producing an agglomerate in dry form; adding an organic solvent to the dry agglomerate producing a clay; callendering the clay into a thin sheet with a thickness less than 1mm, forming an active layer or gas diffusion layer, one or both layers containing a current collector; and combining said active
25 layer and said gas diffusion layer forming the gas diffusion electrode.

In an embodiment the method includes agglomerating using a ball mill for mixing. The powders are then mixed for more than 30 min. Agglomerating may in an even further embodiment be performed using a blender for mixing with rotating knives at
30 1000-3000 rpm. The powders are heating prior to agglomerating to a temperature in the range 50-200°C. The agglomeration time is in this embodiment at least 1 minute. It is also possible to perform agglomeration using a high-speed mill with rotating blades at more than 10000 rpm. The agglomeration time is in this embodiment from 10 seconds to 5 minutes.

The solvent may be slowly added to the agglomerate under stirring. The agglomerate may be heated during stirring. The method may in another embodiment comprise extruding the clay into a thin film prior to callendering. A current collector or mechanical support may be callendered into the film.

The powder mixture forming the active layer may comprise 100 wt% graphite. Alternatively, the powder mixture forming the active layer may comprise 25-75 wt% graphite with platinum, and 25-75 wt% graphite. In an even further embodiment the powder mixture forming the active layer comprises 25-75 wt% graphite with Ag, Co, Fe, various perovskites or spinells as a catalyst, and 25-75 wt% graphite. PTFE with a particle size less than 1mm may be added to the mixture before agglomerating. The powder mixture providing the gas diffusion layer may comprise 55-75 wt% activated carbon or graphite and 25-45 wt% PTFE.

In a further callendering step said electrode may be callendered with a further gas diffusion layer. The layers in the electrode may be combined by callendering or pressing. The electrode may further be dried at a temperature less than 40°.

The method above is performed in a continuous production line, and the gas diffusion layer and the active layer may be produced in parallel continuous production lines, said production lines being combined in the combining step.

In a further aspect the invention provides an electrode manufactured by the method described above.

In an even further aspect the invention provides a gas diffusion electrode comprising a gas diffusion layer and an active layer, the gas diffusion layer comprising 55-75 wt% activated carbon or graphite and 25-45 wt% PTFE and the active layer comprising 25-75 wt% activated carbon or graphite with noble or non-noble catalyst and 25-75 wt% activated carbon or graphite with high surface area ($>100 \text{ m}^2/\text{g}$) and 5-20 wt% PTFE, the gas diffusion layer and the active layer being manufactured according to the method described above.

The gas diffusion electrode produced by the method above, may be used in fuel cells, metal-air batteries or membranes.

In the production method described above the advantage of the dry method and the wet methods are combined, to give gas diffusion electrodes with high activity and good stability, in a continuous production line without the need of heat treatment. Oxygen electrodes and hydrogen electrodes with high reaction rates and long lifetime stability have been developed by the described method. The production method is simple and does not include any high temperature steps or hazardous chemicals. As shown in Figure 1 the method can be used in a continuous production line.

By the use of porous electrodes the oxygen reaction and the hydrogen reaction can be performed with high efficiency. Porous electrodes are often made with two layers. One gas diffusion layer preventing liquid penetration into the gas chamber, and one active layer where the reaction takes place. The two layers are rolled or pressed together to form the electrode. The porous active layer gives a large surface area available and thus high reaction rates.

The active layer is produced with a double pore structure. Hydrophobic pores are used to transport gas into the electrode from the gas chamber. From the electrolyte side hydrophilic pores are filled with the liquid electrolyte. Inside the electrode the reaction takes place on the 3-phase boundary. The main challenge in the production of the electrodes is to make electrodes with both high activity and good stability (> 2000 h).

BRIEF DESCRIPTION OF DRAWINGS

Embodiments of the invention will now be described with reference to the following drawings, in which:

Figure 1 shows a continuous production line for manufacturing a thin gas diffusion electrode according to an embodiment of the invention;

Figure 2 shows oxygen reduction from air at 20 °C of electrodes with and without a noble metal catalyst;

Figure 3 shows a graph of lifetime of electrode for oxygen reduction from air at 70 °C at 100 mA/cm² in a galvanostatic experiment at 0,1 A/cm²; and

Figure 4 shows a gas diffusion electrode manufactured according to an embodiment of the invention, comprising an active layer and a gas diffusion layer with a mesh current collector inside the gas diffusion layer.

DETAILED DESCRIPTION

Figure 1 shows a continuous production line for manufacturing a thin gas diffusion electrode according to an embodiment of the invention. The production line consists in four main steps. (I) a milling and agglomeration step, (II) a mixing step, (III) an extruding step and (IV) a callendering step. However, the extruding step may be omitted and the clay formed in step (II) may be forwarded directly into the callendering step. As shown in Figure 1 parallel production lines for production of different layers are set up, and the layers can be combined in a step (V) forming an electrode with an active layer and a gas diffusion layer. The different steps will be explained in detail below.

(I) Agglomeration:

As shown in Figure 1 the first step (I) in the electrode production is the agglomeration of the powder mixture. In Figure 1 the powder mixture consists in three powders A, B and C. The powders A, B and C are examples only and fewer or more powders may be used. To prevent the removal of surfactants by heat treatment the powder mixture is agglomerated with PTFE particles in the dry form.

Three agglomeration methods are possible:

1. A ball mill is used. The powders are mixed for more than 30 min to obtain a homogeneous agglomerate.
2. A commercially available blender is used with rotating knives at 1000-3000 rpm. Prior to mixing, the powders are heated in the range 50-200 °C. The agglomeration time should be at least 1 minute.
3. A high-speed mill is used with rotating blades at more than 10000 rpm. The high rotating speed results in rapid agglomeration, and pre-heating of the powders is not necessary to obtain good agglomerate. The agglomeration time is from 10 seconds to 5 minutes.

(II) Clay formation:

Figure 1 part (II) shows the unit for clay formation from the agglomerate. To overcome the severe problems of continuous production from the dry agglomerate, an organic solvent is added after the agglomeration. The agglomerate is then transformed into a clay, which can easily be made into a thin layer. By adding the solvent, after the agglomeration step in the production, wetting agents does not have to be used.

The clay is formed by slowly adding the solvent to the agglomerate under stirring. In this manner the solvent is baked into the agglomerate and a homogeneous clay is formed. In some cases, especially with the use of a low PTFE content (<10 wt%) or with materials that agglomerate poorly, it is important to plastify the clay further, in such cases the solvent and/or the clay can be heated under the baking process.

By this method the problem with the PTFE coverage of any unnecessary large surface of the mass particles by plastified binders as explained earlier in background, is avoided. This means that high electrocatalytic activity is obtained. In addition no high temperature steps are needed.

By adding the organic solvent after the agglomeration is formed the good properties of a clay in a continuous production line is employed. In this manner the best qualities of the dry and the wet production method are utilised to form a method for cost effective continuous production of gas diffusion electrodes.

Extrusion

Figure 1 part (III) shows the extrusion unit. In order to reduce the amount of callendering steps an extrusion unit is used. The clay is then extruded into a thin film. This step may be omitted, but it is often used to simplify the callendering.

Callendering

Figure 1 part (IV) shows the callendering of the clay. The objective of the callendering is to make a film of uniform thickness. In addition a current collector or mechanical support can be callendered into the film.

The gas diffusion electrode can be made of two layers, an active layer and a gas transport layer. In the active layer the reaction takes place. This layer must have a double pore structure for gas- and liquid transport to the reaction sites. An additional diffusion layer is used to prevent liquid from entering the gas chamber. This layer must have sufficient gas transport properties and high hydrophobisity. Both these layers can be made in the method described above by the agglomeration, clay formation, extrusion and callendering steps. This is shown in Figure 1 as parallel production lines combining in step (V) forming the electrode. Powders A and D are shown as illustrations only in Figure 1 for the below production line, and only one or more than two powders may be used.

As shown in Figure 1 part (V) the two layers are combined in a callendering step. With good extrusion, callendering may be omitted for the individual layers and only one callendering step used to bind the two layers and the current collector together. Pressing can also combine the two layers. The current collector and/or mechanical strength support material can be callendered or pressed into the gas diffusion layer and/or into the active layer and/or between the two layers as illustrated in Figure 1.

A possible assembly of the gas diffusion electrode produced by the method described above is shown in Figure 4. Reacting gases are transported through the gas diffusion layer and into the active layer. The active layer is partially filled with the electrolyte. Within the active layer the reaction takes place on the three phase boundary between the gas phase, the liquid phase and the catalyst particles.

EXAMPLES

According to the method of the invention gas diffusion electrodes have been made and tested. Gas diffusion electrodes consist of two layers named the active layer and the gas diffusion layer. In addition a woven, etched or expanded mesh is pressed or rolled into the gas diffusion electrode.

Figure 2 shows the catalytic activity of two gas diffusion electrodes, one with a noble-metal catalyst and the other without a noble metal catalyst. The electrodes have been prepared by the method described in the invention. The electrode without noble metal catalyst was prepared with the use of 15 wt% PTFE and 85 wt% high surface area graphite. The surface area of the graphite must be $> 100 \text{ m}^2/\text{g}$. The use of graphite instead of high surface area active carbon is necessary to give long lifetime of the electrodes, however some forms of active carbon may be used.

Figure 3 shows the lifetime study of a gas diffusion electrode with graphite for oxygen reduction. At a current of $100 \text{ mA}/\text{cm}^2$ and a temperature of 70°C the potential is stable for more than 1400 hours. As shown in the figure, long lifetime is obtained with the use of graphite. This is related to the degradation mechanism of the electrodes. Degradation of gas diffusion electrodes for oxygen reduction is caused by radicals formed in the reaction. These radicals attack the carbon, increasing the hydrophilicity of the electrode and causing flooding of the structure. With graphite, the attacks by radicals are less severe as graphite is more stable than active carbon. High surface area is necessary to create the pore structure for gas and liquid transport. Therefore, the use of high surface area graphite is optimal. The same effect may however also be obtained with some types of active carbon that are especially stable, for instance carbons with a high number of basal planes in the surface structure.

Figures 2 and 3 show high electrocatalytic activity and long lifetime, which is obtained due to the preparation method described in the invention. Lifetimes for common electrode production methods should exceed 1000 hours to be of commercial interest. The electrodes produced according to the methods described in this invention are stable for more than 10 000 hours. Also shown in Figure 2 is an electrode with catalyst. This increases the catalytic activity towards the oxygen reaction. In the figure, graphite with 5 wt% Pt was used for the active layer. To maintain high stability with the high reaction rates on the platinum sites, a graphite support for the catalyst must have a surface area ($< 50 \text{ m}^2/\text{g}$). Other non-noble catalysts may also be used on the graphite support for oxygen reduction, for instance

Ag, Co, Fe or various perovskites and spinells. In addition a high surface area ($>100 \text{ m}^2/\text{g}$) graphite or activated carbon must be added to give the correct pore structure.

5 As shown, it is important to use the correct types of carbons and/or graphite in order to obtain high activity and long lifetime. For the active layer studies have shown that a mix of 25 to 75 wt% graphite with 5 wt% Pt (BET surface area $10 \text{ m}^2/\text{g}$) and 25 to 75 wt% Timrex HSAG300 graphite from Timcal with BET surface of $280 \text{ m}^2/\text{g}$ gives high activity ($> 150 \text{ mA}/\text{cm}^2$ at 1 V vs. Zn) and stability
10 ($> 2000 \text{ h}$). Samples with only Timrex HSAG300 also show high reaction rates ($>100 \text{ mA}/\text{cm}^2$ at 1 V vs Zn) and good stability. Before agglomeration PTFE (5-25 wt%) with a particle size of $< 1 \text{ mm}$ was added to the carbon powders.

For the gas diffusion layer our studies have shown that graphite from Timrex (e.g.
15 HSAG300) or activated carbon from Cabot (e.g. Vulcan X72) can be used. Before agglomeration 25-45 wt% of PTFE with a particle size of $< 1 \text{ mm}$ was added to the carbon powder. This gives a gas diffusion layer with high conductivity and hydrophobisity. With 35 wt% PTFE high hydrophobisity and conductivity in the gas diffusion layer is obtained.

20

Agglomeration:

Agglomeration is performed in the same manner for the active- and the gas diffusion layer. Adding PTFE to the carbon powder mix produces the agglomerate. The agglomeration was performed in a high-speed mill (20 000 rpm) for 1 min. The advantage of the high-speed mill is the rapid agglomeration from dry powders. With
25 no surfactants (wetting agents) the hydrophobisity of the agglomerate is high.

In order to make a thin sheet electrode from the agglomerate a hydrocarbon solvent is used, for instance Shellsol. It is added and by slow stirring a clay was
30 formed.

Callendering

The clay can be extruded and callendered into a thin sheet ($< 1 \text{ mm}$ thick). A Ni-mesh current collector was callendered into the thin electrode sheet. Also, other

materials can be used for the current collector e.g. Ag, silver coated copper, nickel coated copper or carbon composite materials. Alternatively, the current collector can be callendered into the gas diffusion layer. The callendering procedure is performed in the same manner for the gas diffusion layer and the active layer.

5

Gas diffusion electrode production:

To form the gas diffusion electrode the active- and the gas diffusion layer must be combined. The current collector was callendered into the gas diffusion layer prior to combining it with the active layer. The two layers were combined by callender-
 10 ing them together. After the active layer was rolled together with the gas diffusion layer, the electrode was dried at $< 40^{\circ}\text{C}$ to evaporate the solvent. The total thickness of the two-layer electrode should be (400-1000 μm).

The high reaction rates of gas diffusion electrodes are obtained by a large surface
 15 area of the 3-phase boundary. However, for the use in commercial products, such as fuel cells or metal-air batteries, several other conditions must be granted. High stability of the electrodes is essential. The production method must allow rapid production at a low costs. In addition the electrodes must be easy to handle and store. The presented invention gives a rapid production method of gas diffusion
 20 electrodes that enables the use low cost materials. The electrodes are produced with high electrocatalytic activity and stability. The high mechanical strength enables easy handling and storage of the electrodes.

Having described specific embodiments of the invention it will be apparent to those
 25 skilled in the art that other embodiments incorporating the concepts may be used. These and other examples of the invention illustrated above are intended by way of example only and the actual scope of the invention is to be determined from the following claims.



C L A I M S

1. Method of manufacturing a gas diffusion electrode, the method comprising:
 - a) agglomerating a powder mixture with PTFE particles in a dry form producing an agglomerate in dry form;
 - b) adding an organic solvent to the dry agglomerate producing a clay;
 - c) callendering the clay into a thin sheet with a thickness less than 1mm, forming an active layer or gas diffusion layer, one or both layers containing a current collector; and
 - d) combining said active layer and said gas diffusion layer forming the gas diffusion electrode.
2. Method according to claim 1, characterized in agglomerating using a ball mill for mixing.
3. Method according to claim 2, characterized in mixing the powders for more than 30 min.
4. Method according to claim 1, characterized in agglomerating using a blender for mixing with rotating knives at 1000-3000 rpm.
5. Method according to claim 4, characterized in heating the powders prior to step a) to a temperature in the range 50-200°C.
6. Method according to claim 4, characterized in an agglomeration time of at least 1 minute.
7. Method according to claim 1, characterized in agglomerating using a high-speed mill with rotating blades at more than 10000 rpm.

8. Method according to claim 7,
characterized in that the agglomeration time is from 10 seconds to
5 minutes.

5 9. Method according to claim 1,
characterized in slowly adding the solvent to the agglomerate under
stirring.

10 10. Method according to claim 9,
characterized in heating the agglomerate during stirring.

11. Method according to claim 1,
characterized in extruding the clay into a thin film prior to callendering.

15 12. Method according to claim 1,
characterized in callendering a current collector or mechanical support
into said film.

20 13. Method according to claim 1,
characterized in that the powder mixture forming the active layer compris-
ing 100 wt% graphite.

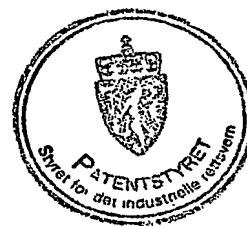
25 14. Method according to claim 1,
characterized in that the powder mixture forming the active layer compris-
ing 25-75 wt% graphite with platinum, and 25-75 wt% graphite.

30 15. Method according to claim 1,
characterized in that the powder mixture forming the active layer compris-
ing 25-75 wt% graphite with Ag, Co, Fe, various perovskites or spinells, and
25-75 wt% graphite.

16. Method according to claim 1,
characterized in adding PTFE with a particle size less than 1mm to the
mixture before agglomerating.

17. Method according to claim 1,
characterized in that the powder mixture comprising 55-75 wt% activated
carbon or graphite and 25-45 wt% PTFE providing the gas diffusion layer in
5 step c).
18. Method according to claim 1,
characterized in a further callendering step callendering said electrode
with a further gas diffusion layer made in steps a)-d).
- 10 19. Method according to claim 1,
characterized in combining said layers by callendering or pressing.
20. Method according to claim 1,
15 characterized in drying said electrode at a temperature less than 40°C.
21. Method according to claim 1,
characterized in performing said steps a)-d) in a continuous production
line.
- 20 22. Method according to claim 1,
characterized in producing said gas diffusion layer and said active layer
in parallel continuous production line and combining said production lines in the
combining step.
- 25 23. Electrode manufactured by the method according to claims 1-21.
24. Gas diffusion electrode comprising a gas diffusion layer and an active layer,
the gas diffusion layer comprising 55-75 wt% activated carbon or graphite and
30 25-45 wt% PTFE and the active layer comprising 25-75 wt% activated carbon or
graphite with noble or non-noble catalyst and 25-75 wt% activated carbon or grap-
hite with high surface area ($>100 \text{ m}^2/\text{g}$) and 5-20 wt% PTFE, the gas diffusion
layer and the active layer being manufactured according to the method in claim 1.

25. Use of the gas diffusion electrode produced by the method according to claim 1 in fuel cells, metal-air batteries or membranes.



ABSTRACT

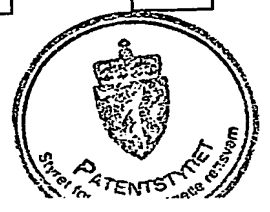
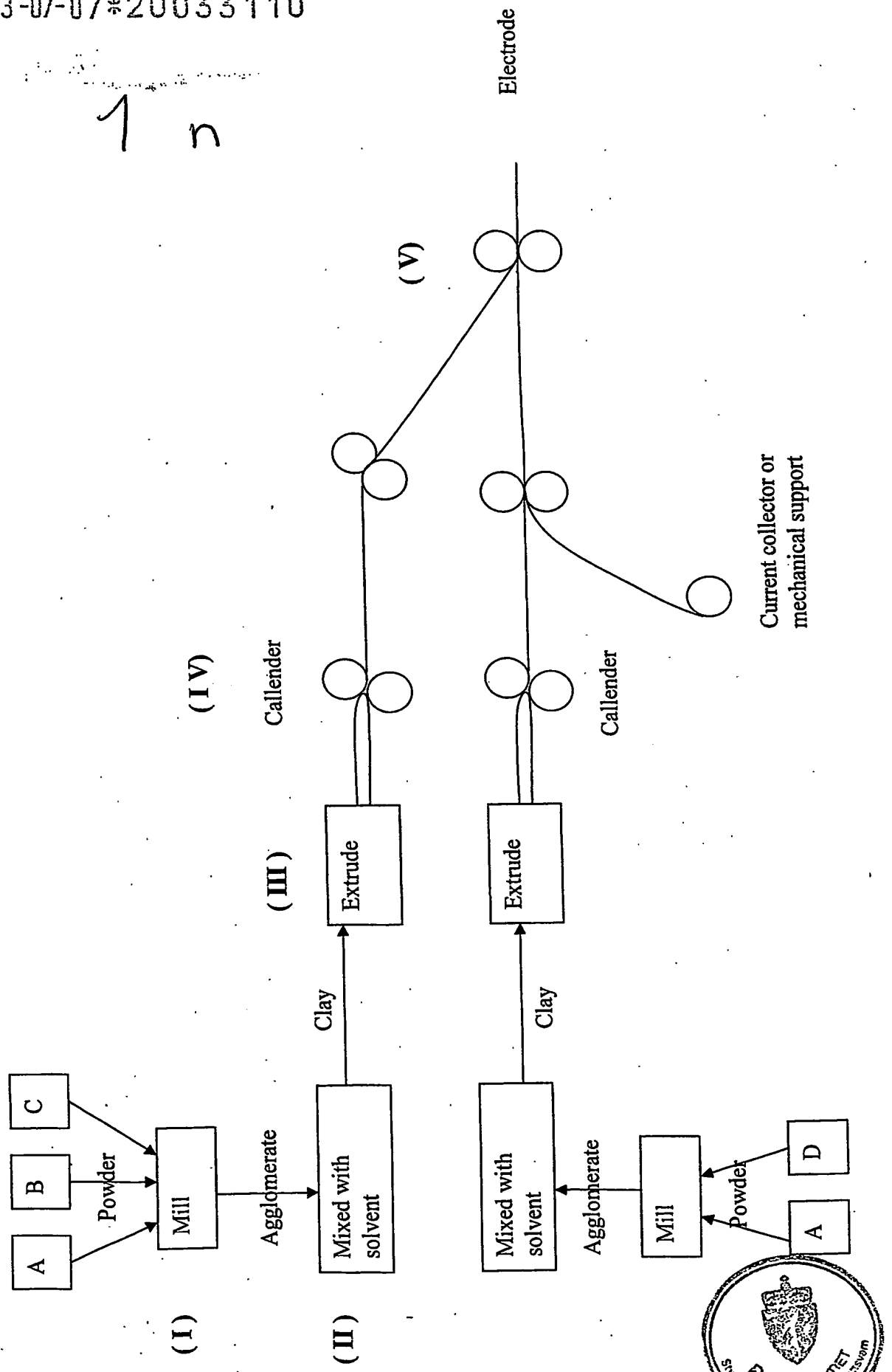
A method for production of a gas diffusion electrode is described, and especially a method for producing a plastic bounded thin gas diffusion electrode with high catalytic activity for the oxygen or the hydrogen reaction. The method comprising the following steps: agglomerating a powder mixture with PTFE particles in a dry form producing an agglomerate in dry form; adding an organic solvent to the dry agglomerate producing a clay; callendering the clay into a thin sheet with a thickness less than 1mm, forming an active layer or gas diffusion layer; in which one or both contain a current collector; and combining said active layer and said gas diffusion layer forming the gas diffusion electrode. The produced gas diffusion electrode may be used in e.g. fuel cells, metal-air batteries or membranes.

15

Figure 1



Figure 1



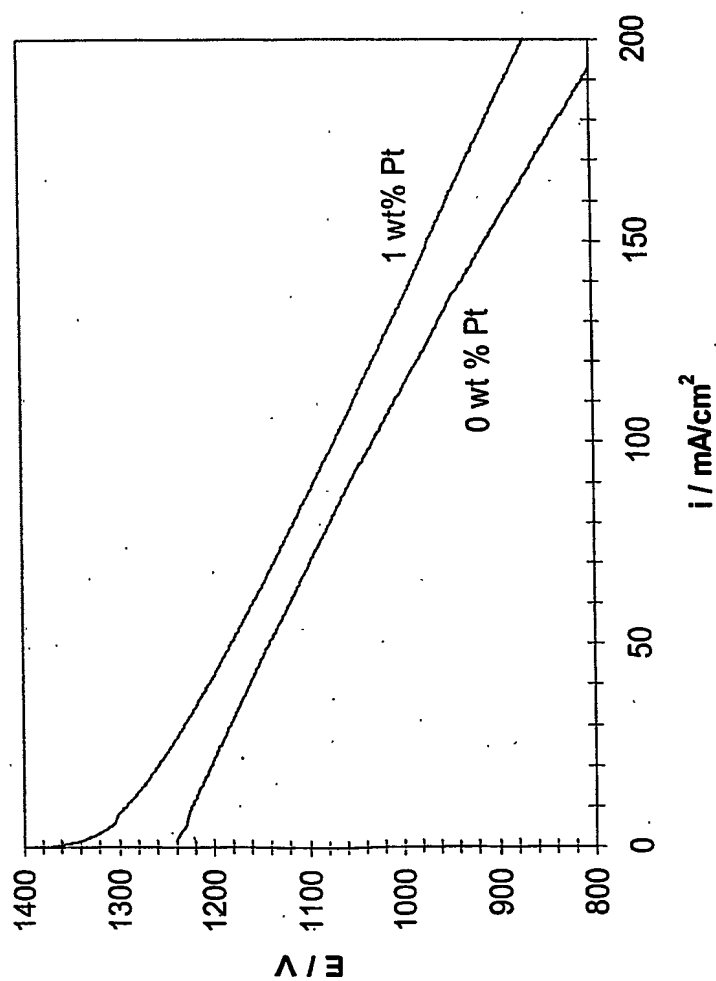
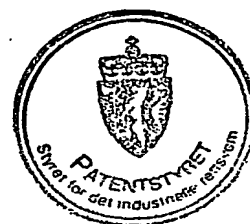


Figure 2. Oxygen reduction from air at 20 °C of electrodes with and without noble metal catalyst.



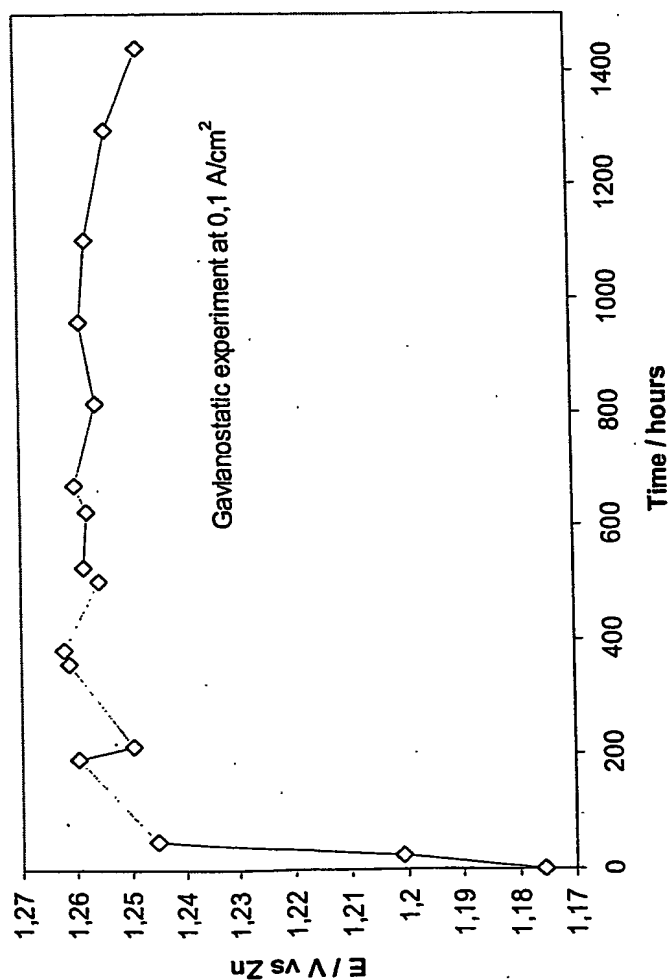
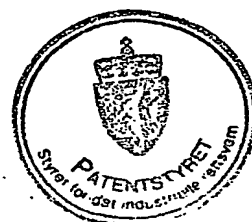


Figure 3. Lifetime of electrode for oxygen reduction from air at 70 °C at 100 mA/cm²



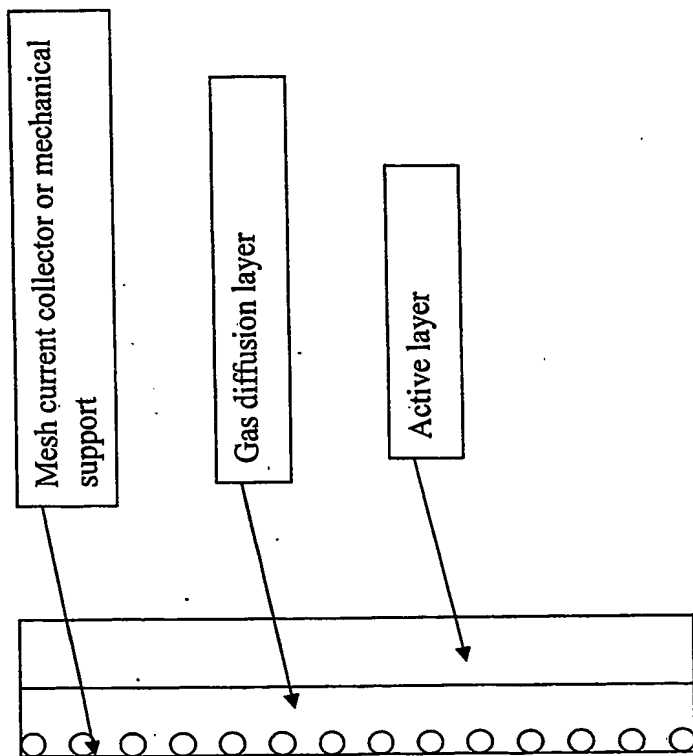


Figure 4

